Component 1 was collected by preparative glpc and identified as *trans*-**20** (or *cis*-**20**): ir (neat) 1740 (ester C=O), 1660 (C=C), 1440, 1366, 1175, 1110, 1040, 990, 830, 790 cm^{-1}; nmr (CCl$_4$) δ 2.08 (s, 3, CH$_2$CCl=), 2.33 (broad s, 4, –CH$_2$CH$_2$), 3.62 (s, 3, –CO$_2$CH$_3$), 5.51 ppm (broad s, 1, –CH=); mass spectrum (70 eV) *m/e* (rel intensity) 162 (19, M$^+$, 1 Cl), 131 (76), 127 (100, M$^+$ – Cl), 105 (61), 104 (60), 103 (68), 102 (75), 95 (57), 89 (72), 85 (68), 74 (61), 67 (63), 59 (50), 53 (61).

Anal. Calcd for $C_7H_{11}ClO_2$: C, 51.70; H, 6.82. Found: C, 51.58; H, 6.72.

Component 2, collected similarly, was identified as *cis*-**20** (or *trans*-**20**): ir (neat) 1740 (ester C=O), 1660 (C=C), 1440, 1366, 1340, 1175, 1110, 1080, 1035, 990, 860, 830, 800 cm.$^{-1}$ The nmr (CCl$_4$) and mass spectrum (70 eV) of this component were like those of component 1.

Anal. Calcd for $C_7H_{11}ClO_2$: C, 51.70; H, 6.82. Found: C, 51.43; H, 6.60.

Reaction of 8 with Sodium Methoxide in Dry Methanol.—To a stirred solution of 5.9 g (0.11 mol) of sodium methoxide in 25 ml of dry methanol was added dropwise at 34–45° a solution of **8** (3 g, 0.018 mol) in 6 ml of dry methanol, for a period of 10 min. The mixture was stirred for additional 15 min, and poured into a large amount of water. The organic layer was extracted with ether, washed with water, and dried over MgSO$_4$. Removal of the solvent left 1.4 g of a light yellow, clean oil, bp 75–78° (12 mm). Glpc analysis (column B, 120°, carrier gas N$_2$, 0.5 kg/cm^2, 42 ml/min) of this oil showed three peaks. The peaks, retention times (min), and integrated percentages are as follows: 1, 3.2, 28%; 2, 4.7, 60%; 3, 6.2, 11%. Component 1 was collected by preparative glpc and identified as methyl sorbate (**21**) by comparison of the infrared spectrum and retention time with those of methyl sorbate prepared by the esterification of sorbic acid with diazomethane: yield 17%; ir (neat) 1723 (ester C=O), 1650 (C=C), 1623 (C=C), 1010 cm^{-1} (=CH);[10] nmr (CCl$_4$) δ 1.85 (d, 3, J = 5.5 Hz, –CH$_3$), 3.67 (s, 3, –CO$_2$CH$_3$), 5.69 (d, 1, J = 16 Hz, C-2 H), 6.20 (m, 2, C-4 H and C-5 H), 7.16 ppm (m, 1, C-3 H).[9]

Components 2 and 3 were collected and identified as *trans*-**20** (or *cis*-**20**) (yield 29%) and *cis*-**20** (or *trans*-**20**) (yield 5%), respectively, by comparison of ir spectra and retention times with those of an authentic sample.

Reaction of 8 with Sodium Methoxide in Aprotic Solvents (Ether, Benzene, and *n*-Hexane).—To a suspension of 0.76 g (0.014 mol) of sodium methoxide in 10 ml of aprotic solvent was added 0.88 g (0.0048 mol) of **8** in several portions during the course of 5 min, at 0° with stirring. After the mixture was stirred at 0–10° for a further 30 min, it was worked up in the usual manner. The composition of the products was determined by glpc (column B, 120°, carrier gas N$_2$, 0.5 kg/cm^2, 42 ml/min).

Transformation of the Ester 20 to the Ester 21 with Sodium Methoxide.—To a mixture of sodium methoxide (0.14 g, 0.0025 mol) and dry ether (1 ml) was added a solution of **20** (0.082 g, 0.0005 mol) in dry ether (1 ml) at 0°. The mixture was stirred for 30 min and filtered. Removal of the solvent gave 0.04 g of a clean oil. Glpc analysis (column A, 120°, carrier gas N$_2$, 0.5 kg/cm^2, 42 ml/min) indicated this oil to contain three components, which were identified by the comparison of the retention times with those of the authentic samples. Peaks, compounds, retention times (min), and the integrated peak areas are as follows: 1, **21**,[21] 3.3, 9%; 2, *trans*-**20** (or *cis*-**20**), 4.2, 61%; 3, *cis*-**20** (*trans*-**20**), 5.1, 30%.

Registry No.—**1**, 1552-26-7; **2**, 1552-33-6; **3**, 22970-18-9; **7**, 38666-05-6; **8**, 38666-06-7; **9**, 38666-07-8; **10**, 38666-08-9; **11**, 38666-09-0; **12**, 38666-10-3; **14**, 38666-11-4; **18**, 21651-12-7; **19**, 38666-13-6; (*Z*)-**20**, 38666-14-7; (*E*)-**20**, 38666-15-8; **21**, 1515-80-6; ethyl acetoacetate, 141-97-9; dichloroacetaldehyde, 79-02-7; acetylacetone, 123-54-6; 2,2-dichloropropanol, 27313-32-2.

[21] Yield 6%.

Determination of Stereochemistry in Vinyl Phosphorylated Species by Nuclear Magnetic Resonance Shift Reagents. Revised Mechanistic Pathways for the Perkow Reaction[1]

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The application of lanthanide induced shifts employing Eu(DPM)$_3$ [and, to a minor extent, Pr(DPM)$_3$], to the nmr spectra of di-, tri-, and tetrasubstituted vinyl phosphates, phosphonates, and phosphinates is described. Vicinal cis protons or methyl groups undergo greater shifts than the corresponding trans groups. On this basis, *E* and *Z* stereochemical assignments can be made for such groups. The major isomers in the *gem*-phenyl vinyl phosphorylated compounds featuring vicinal phenyl, methyl, bromine, or chlorine groups are shown to be *Z*, reversing our previous assignments. Confirmation of this assignment is found by a positive nuclear Overhauser effect from phenyl to vicinal proton on the major (*Z*) isomer of diethyl 1-phenyl-2-chlorovinylphosphate. Available stereochemical data, including these revised results and the tendency toward smaller *Z/E* ratios in Perkow reactions involving alkyl diphenylphosphinites, compared with trialkyl phosphites, are evaluated on the basis of variations of the carbonyl addition mechanism previously proposed. The Perkow reactions of α,α-dibromo ketones and α-bromo-α-phenyl ketones, which give only *Z* vinyl phosphorylated products, may occur *via* halogen attack. The importance of considering the magnitude of k_2 Br/Cl ratios for pairs of bromo and chloro ketones, as well as *E,Z* stereochemistry of the products, in evaluating the various mechanistic pathways for the Perkow reaction, is stressed.

We have recently reported the determination of the relative stereochemistry of the *E* and *Z* isomeric vinyl phosphates arising from the Perkow reaction of α-halo ketones with trialkyl phosphites,[2,3] Of the various methods used,[2] the most reliable *seemed* to be the use of nmr additive increments as developed by Simon and Sternhell[4] and modified by Tobey.[5] This method correctly assigns *E* and *Z* stereochemistry to isomeric di- and trisubstituted olefins in a large number of cases.

We now find that in the case of trisubstituted *gem*-phenyl vinyl phosphates (and the related phosphinates and phosphonates[6]) the *E* and *Z* assignments by

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[1] This investigation was supported by Grant No. 19,664 from the National Science Foundation. This is Organophosphorus Chemistry. 23.

[2] I. J. Borowitz, S. Firstenberg, E. W. R. Casper, and R. K. Crouch, *J. Org. Chem.*, **36**, 3282 (1971).

[3] I. J. Borowitz, S. Firstenberg, G. B. Borowitz, and D. Schuessler, *J. Amer. Chem. Soc.*, **94**, 1623 (1972).

[4] (a) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966); (b) U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969); (c) U. E. Matter, *et al.*, *ibid.*, **25**, 2023 (1969).

[5] S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).

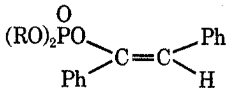
[6] I. J. Borowitz and R. K. Crouch, *Phosphorus*, **3**, 3 (1973).

these calculations are close in value and give the reversed assignment; *i.e.*, the actual stereochemistry is the opposite (see below). If the correct assignments are compared with the calculated values (Table I), the vinyl proton of the *E* isomers is found to be abnormally deshielded. Perhaps this is due to a decreased mesomeric effect of the phosphate group when it is part of a "buttressed" system (phosphate, *gem*-phenyl, R cis to phenyl) which does not allow the vinyl oxygen to be properly oriented for the usual shielding effect noted.[2]

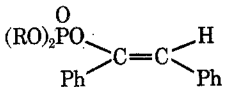
TABLE I
CALCULATION OF VINYL PROTON NMR ABSORPTION IN *gem*-PHENYL VINYL PHOSPHATES[a]

Compd	Isomer	Vinyl proton [$\delta(CCl_4)$]		
		Obsd	Calcd	
1a	Major, *Z*	6.33	6.49	(6.38)[b]
1b	Minor, *E*	6.69	6.33	
2a	Major, *Z*	5.60	5.60	(5.49)[b]
2b	Minor, *E*	5.77	5.35	
3a	Major,[c] *Z*	6.13	6.14	(6.03)[b]
3b	Minor,[c] *E*	6.45	5.96	
4a	Major, *Z*	6.14	6.18	(6.07)[b]
4b	Minor, *E*	6.49	5.93	

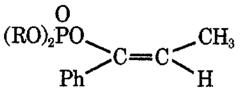
[a] R = C_2H_5. [b] Revised values using $Z_{trans} = 0.61$, based on **11b**, **13**, and **15**. Revision suggested by a referee. [c] Isomer ratio obtained in original Perkow reaction. Distillation reverses the isomer ratio.



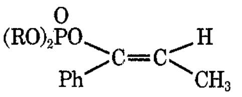
1a



1b



2a



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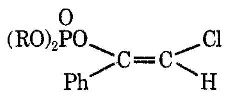
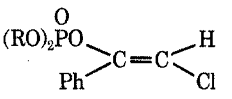
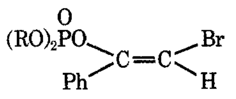


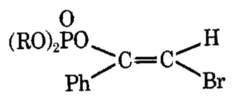
3a



3b



4a



4b

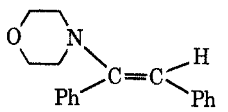
Allylic substitution next to a vinyl phenyl results in abnormal deshielding of vicinal vinyl protons, a related phenomenon.[4c]

In contrast, the additive increment method correctly predicts the nmr absorption of the vinyl protons in the *E,Z* isomeric pairs of substituted stilbenes containing morpholino[7a] and butyl[7b] groups (Table II). Thus stilbenes are not abnormal *per se*.

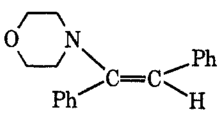
TABLE II
CALCULATION OF VINYL PROTON NMR ABSORPTION IN STILBENES

Compd	Registry no.	Vinyl proton (δ)	
		Obsd	Calcd[a]
i	4176-69-6	5.56[b]	5.32
ii	4176-68-5	5.71[b]	5.80
iii	5041-39-4	6.38[c]	6.36
iv	5041-40-7	6.64[c]	6.73

[a] From group increment values in ref 4b. [b] In cyclohexane.[7a] [c] In $CHCl_3$.[7b]



i



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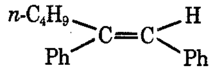
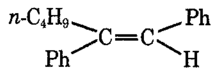


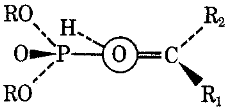
iii



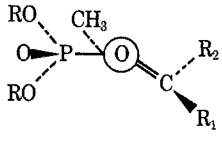
iv

Determination of Vinyl Phosphate Stereochemistry by Lanthanide Induced Shifts (LIS).—The use of tris(dipivalomethanato)europium(III) [Eu(DPM)$_3$] in causing lanthanide induced shifts in phosphates has been established.[8] It is generally agreed that the interaction involves coordination of the europium with the PO bond.[8a,c] Table III indicates LIS data obtained on di- and trisubstituted vinyl phosphates, phosphonates, and phosphinates. The data for compounds of known stereochemistry (the cyclic **5**–**9** and acyclic **10**–**12**) indicates the following order of decreasing proton sensitivity [shift, hertz/mole of Eu(DPM)$_3$]: *gem*-vinyl H > cis *vic*-vinyl H $\cong$ CH_2 of ethoxy > trans *vic*-vinyl H $\geqq$ CH_3 of ethoxy. The sensitivity values do not differ greatly for the various groups on phosphorus for a given ethylene. The values for genuine cis vicinal protons[2] (335 for **12**, 375 for **10**] are closer to the assigned cis vicinal proton in acyclic cases such as **11** or **16** than to the trans protons.[9]

These observations suggest that, at least in the presence of Eu(DPM)$_3$, the vinyl phosphorylated species are either all in approximately the same geometrical configuration or that the same averaging of several configurations occurs in all cases. Inspection of Dreiding models indicates that, in most (but not all) of the possible rotational configurations for the PO group relative to the plane of the ethylene moiety, the cis vicinal proton is closer to it than is the trans vicinal proton. This is especially so for the preferred configurations v and vi for geminal proton and *gem*-methyl vinyl phosphates calculated by Gaydou from $^4J_{PH}$ coupling constants.[10] Although the exact position of the europium relative to the PO group is unknown, making the angular term in the usual shift equations[8b] difficult to evaluate, it seems reasonable that larger shifts will be associated with *vic*-vinyl protons which are cis to phosphate. The results for **1a** and **1b** (and dimethyl esters **20a** and **20b**) were confirmed with Pr(DPM)$_3$ which gave greater upfield shifts for **20b** (Table III).



v



vi

The method can be extended to tetrasubstituted

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(7) (a) M. E. Munk and Y. K. Kim, *J. Org. Chem.*, **30**, 370 (1965); (b) J. E. Mulvaney, Z. G. Garlund, and S. L. Garlund, *J. Amer. Chem. Soc.*, **85**, 3897 (1963).

(8) (a) K. C. Yee and W. G. Bentrude, *Tetrahedron Lett.*, 2775 (1971); (b) R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11**, 675 (1972); (c) J. K. M. Sanders and D. H. Williams, *Tetrahedron Lett.*, 2813 (1971); (d) J. R. Corfield and S. Trippett, *Chem. Commun.*, 721 (1971).

(9) The variation of the magnitude of LIS for H_{cis} (and other protons) with various structural features remains to be investigated.

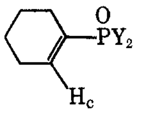
(10) E. Gaydou, *Tetrahedron Lett.*, 4473 (1972).

TABLE III

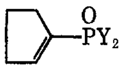
LANTHANIDE INDUCED SHIFTS IN PROTON NMR SPECTRA OF VINYL PHOSPHORYLATED SPECIES[a]

	Magnitude of induced shift (hertz/mole ratio)[b]							
	Vinyl proton							
Substrate	H_{cis}	H_{trans}	H_{gem}	POCH	POCCH	Other groups	$\Delta_{obsd}^{POCH}/\Delta_{obsd}^{i}$[c,d]	$\Delta_{obsd}^{POCCH}/\Delta_{obsd}^{i}$[c,d]
5, Y = OC_2H_5	487			488	176	412 (*gem*-CH_2)	1.01	0.36
6, Y = Ph	486							
7, Y = $OCH(CH_3)_2$	500			510	170	400 (*gem*-CH_2)	0.42	
8, Y = Ph	560					370 (*gem*-CH_2)		
9	510			510	170	400	1.00	0.33
10	375		710	570			H_c, 1.81	
							H_g, 0.82	
11a	300		592	525			H_c, 1.71	
							H_g, 0.94	
11b		75		545			H_t, 6.3	
12	335		710	565		22 (CCH_3)	H_c, 1.65	
13	528	192		486	168	304 (*gem*-CH_3)	H_c, 0.92	0.32
							H_t, 2.50	1.00
14, Y = Ph, OC_4H_9	736	184						
15, Y = OC_2H_5	650	180		500	175			
20a, Y = CH_3		225		400			1.66	
1a, Y = C_2H_5		280		580	153		1.99	0.59
20a		−360[e]		−580[e]			1.68	
20b	>225			610			0.67	
	−1220[e,f]			−810[e]			0.67	
16a, Y = Ph		210						
3a, Y = OC_2H_5		198		378	113			
16b, Y = Ph	470							
3b, Y = OC_2H_5	610			627	216			
4a,b, R = C_2H_5		248[g]		475[g]	152[g]			
2a, R = C_2H_5		140			140	260 (vinyl CH_3)		
2b, R = C_2H_5		440			120	40 (vinyl CH_3)		

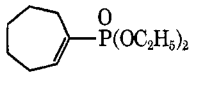
[a] The shifts are downfield and caused by $Eu(DPM)_3$ unless otherwise noted. [b] Obtained from the plots of δ *vs.* mole ratio of $Eu(DPM)_3$/substrate. [c] These ratios are obtained from the slopes of plots of LIS for POCH (or POCCH) *vs.* LIS for vinyl H or vinyl CH_3: D. R. Kelsey, *J. Amer. Chem. Soc.*, **94**, 1764 (1972). [d] Similar ratios are obtained from the values listed in the table. [e] $Pr(DPM)_3$ values. [f] $Eu(DPM)_3$ with **1b** caused vinyl proton to merge with phenyl. [g] Values found on 97:3 mixture of **4a**:**4b**.



5, Y = OC_2H_5
6, Y = Ph



7, Y = $OCH(CH_3)_2$
8, Y = Ph



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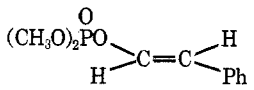

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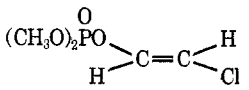

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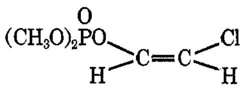

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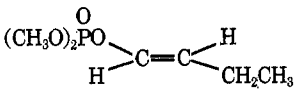

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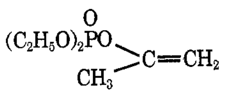

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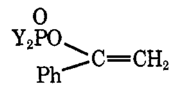
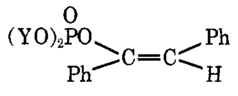
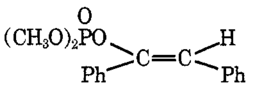


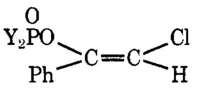
14, Y = Ph, OC_4H_9
15, Y = OC_2H_5



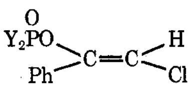
20a, Y = CH_3
1a, Y = C_2H_5



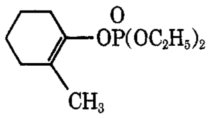
20b



16a, Y = Ph
3a, Y = OC_2H_5



16b, Y = Ph
3b, Y = OC_2H_5



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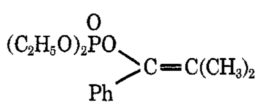

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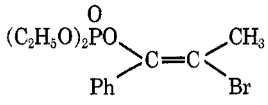
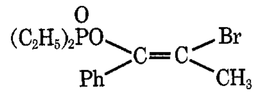


19a



19b

vinyl phosphates bearing methyl groups, whose stereochemistry is not otherwise readily accessible (Table IV). There is good agreement between the shift for the *cis*-methyl group in **17** and the assigned *cis*-methyl groups in **18** and **19**.

Thus the LIS method seems to represent a simple and powerful tool for the determination of *E,Z* stereochemistry in vinyl phosphorylated species.

Further Evidence for the Assignment of *E,Z* Stereochemistry of *gem*-Phenyl Vinyl Phosphorylated Species. —Since the stereochemistry of the *E,Z* pairs **1a,b**–**4a,b** as determined by LIS is opposite to that originally deduced by the Simon–Sternhell calculations,[2] further confirmation of the revised stereochemical assignments was sought. The diethyl 1-phenyl-2-chlorovinylphosphate pair **3** (60:40 ratio of distilled material, changed from the 40:60 ratio of isomers formed in the reaction of dichloroacetophenone with triethyl phosphite) has an upfield vinyl proton doublet which had been assigned as trans to phenyl originally.[2]

TABLE IV

$Eu(DPM)_3$ INDUCED SHIFTS ON VINYL METHYLS IN VINYL PHOSPHORYLATED SPECIES[a]

	Magnitude of induced shift (hertz/mole ratio)[b]						
	Vinyl methyl						
Substrate	*cis*-CH_3	*trans*-CH_3	*gem*-CH_2	POCH	POCCH	$\Delta_{obsd}^{POCH}/\Delta_{obsd}^{i}$ [c,d]	$\Delta_{obsd}^{POCCH}/\Delta_{obsd}^{i}$ [c,d]
17	292		508	490	157	$(CH_3)_c$, 1.67	0.55
18	312	112		495	140	$(CH_3)_c$, 1.59	0.44
						$(CH_3)_t$, 4.28	1.18
19a	322						
19b		108					

[a-d] The same as those in Table III.

TABLE V

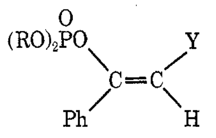
REVISED VINYL PHOSPHATE AND PHOSPHINATE SPECTRAL DATA[a]

		3-Vinyl H nmr				
Compd	Isomer ratio	$-\delta_{Et_2O}$	$\Delta = \delta_{Et_2O} - \delta_{BF_3Et_2O}$	$-\delta_{CCl_4}$	$\Delta = \delta_{CCl_4} - \delta_{C_6D_6}$	$^4J_{POCCH}$, Hz
22						
H_B		5.28	−0.06	5.21	−0.36	2.2
H_C		5.05	−0.29	5.04	+0.07	2.0
(*Z*)-**1a**	65	6.42	−0.28	6.33	−0.15	1.0
(*E*)-**1b**	35	6.79	−0.02	6.69	+0.30	2.5
(*Z*)-**2a**	61–70	5.66	−0.16	5.60	+0.05	2.5
(*E*)-**2b**	30–39	5.79	−0.04	5.77	−0.23	2.8
(*Z*)-**3a**	60	6.31	−0.19	6.13	+0.21	2.3
(*E*)-**3b**	40	6.56	−0.08	6.45	−0.25	2.8
(*Z*)-**4a**	97	6.36	−0.21	6.14	+0.17	1.6
(*E*)-**4b**	3	6.59		6.49	−0.23	2.8

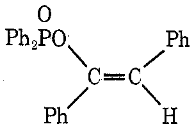
[a] Assignments are reversed from those reported previously in ref 2. The vinyl phosphates and **22** are synthesized from the reaction of triethyl phosphite (or ethyl diphenylphosphinite) with the appropriate α-bromo or chloro ketone (see ref 2 and Table VI).

This proton is now found to be cis to phenyl by a positive nuclear Overhauser effect (NOE) (63:37 of **3b**:**3a** changes to 47:53, a 16% *increase* in area for the vinyl proton of **3a**). The NOE was caused by irradiation at the ortho protons of the phenyl.[11] Thus the upfield proton belongs to the *Z* isomer **3a** and not to the *E* isomer **3b**, as previously believed.[2]

Previous attempts at observing an NOE from phosphorus or from methoxyl to the vinyl protons in either isomer of the *E*,*Z* mixture of dimethyl 1,2-diphenylvinyl phosphate (**20**) had failed.[2]



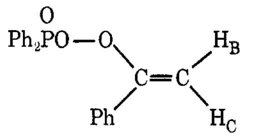
3a, R = C_2H_5; Y = Cl
(*Z*)-**20**, R = CH_3; Y = Ph



21

The mixture of *E*,*Z* stereoisomers **1a**,**b**, the one stereoisomer **1a** (from bromobenzyl phenyl ketone and triethyl phosphite), and the corresponding vinyl phosphinate **21** all have uv absorption at 283 nm which seemed to be more closely related to that of *cis*-stilbene (280 nm) than that of *trans*-stilbene (295 nm).[12] The minor isomer **1b** was separated (by preparative tlc) and was found to have uv absorption at 253 nm, confirming its new assignment as a *cis*-stilbene.

Table V gives data on two other methods previously used in correlating *E*,*Z* stereoisomerism[2] with the now revised structures for **1**–**4**. The β-vinyl protons trans to phosphate show small but significant shielding in benzene, compared to carbon tetrachloride, as expected.[2,13] Only **1** is anomolous. The boron trifluoride coordination of PO causes a greater deshielding of the trans-β-vinyl proton than the *cis*-β-vinyl proton, as observed for other vinyl phosphates and already discussed.[2] Thus these methods would seem to apply to most of the vinyl phosphates studied, including **2**–**4**.[14,15]



22

Revised Stereochemical Course of Perkow Reactions. —Table VI lists the isomer ratios of *gem*-phenyl vinyl phosphorylated species derived from the reaction of various α-haloketones with triethyl phosphite (**25**), dibutyl phenylphosphonite (**24**), and ethyl diphenyl phosphinite (**23**).[6,16] Consideration of this revised data together with other data is summarized as follows.

(*E*)-Vinyl phosphates predominate in the reactions of α-haloaldehydes[2,10] and α-chloroalkyl methyl ketones.[10] (*Z*)-Vinyl phosphates predominate in the Perkow reactions of α-bromoalkyl methyl ketones,[10] β-bromo-α-keto esters,[17] α-haloalkyl phenyl ketones

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[11] Performed on a Varian XL-100 at 100 MHz by Professor J. F. Oth and staff, ETH, Zurich.

[12] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, pp 431–434.

[13] (a) F. Hruska, D. W. McBride, and T. Schaefer, *Can. J. Chem.*, **45**, 1081 (1967); (b) J. Ronague and D. H. Williams, *J. Chem. Soc.*, 2642 (1967); (c) A. Kemula and R. T. Iwamoto, *J. Phys. Chem.*, **72**, 2764 (1968); (d) M. Fetizon, J. Gore, P. Laszlo, and B. Waegell, *J. Org. Chem.*, **31**, 4047 (1966).

[14] The determination of $^3J_{^{13}COH}$ coupling constants in (*E*)- and (*Z*)-vinyl phosphates is in progress by Dr. E. Pretsch, ETH, Zurich.

[15] The X-ray crystal structures of vinyl phosphinates related to **1a** and **4a** are being determined by Professor J. Van derVeen, Stevens Institute of Technology.

[16] R. K. Crouch, Ph.D. Thesis, Yeshiva University, 1972.

[17] (a) J. A. Stubbe and G. L. Kenyon, *Biochemistry*, **10**, 2669 (1971); (b) W. E. Bondinell and D. B. Sprinson, *Biochem. Biophys. Res. Commun.*, **40**, 1464 (1970).

TABLE VI

ISOMER RATIOS OF VINYL PHOSPHORYLATED SPECIES[a]

α-Halo ketone	Tricovalent phosphorus reagent	Isomer ratios	
		Z	*E*
26	**23**	40	60
	24	63	37
	25	61	39
27	**23**	50[c]	50[c]
	24	70[c]	30[c]
	25	70[c]	30[c]
28	**23**	18	82
	24	35	65
	25	60	40
29	**23**	100	0
	24	75	25
	25	65	35
30	**23**	100	0
	24	100	0
	25	100	0
31	**23**	100	0
	25	97	3

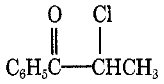
[a] Reaction conditions are given in ref 2, 3, and 6. [b] As determined by ^1H nmr on undistilled and distilled reaction mixtures. A change in isomer ratio upon distillation is noted only for the products **3a** and **3b** (from **28** and **25**). [c] Some ketophosphorylated product is formed in these reactions.[2]

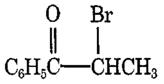
such as **26** and **27**, and other halo and dihalo phenyl ketones (**28**–**31**). In the reactions of **24** and **23** with α-haloalkyl phenyl ketones (**26**–**28**) there is a tendency toward increased *E* isomeric vinyl phosphorylated products *vs.* reactions with **25**. Finally, **30** and **31** give only *Z* products with **23** or **24**.

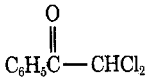
$(C_6H_5)_2POC_2H_5$
23

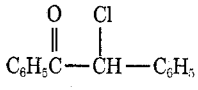
$C_6H_5P(OC_4H_9)_2$
24

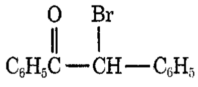
$P(OC_2H_5)_3$
25

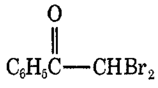

$C_6H_5\overset{O}{\overset{\|}{C}}-\overset{Cl}{\overset{|}{C}}HCH_3$
26


$C_6H_5\overset{O}{\overset{\|}{C}}-\overset{Br}{\overset{|}{C}}HCH_3$
27

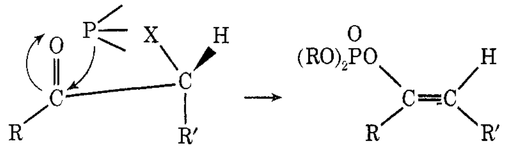

$C_6H_5\overset{O}{\overset{\|}{C}}-CHCl_2$
28


$C_6H_5\overset{O}{\overset{\|}{C}}-\overset{Cl}{\overset{|}{C}}H-C_6H_5$
29

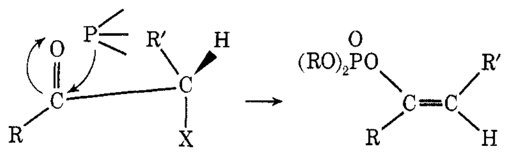

$C_6H_5\overset{O}{\overset{\|}{C}}-\overset{Br}{\overset{|}{C}}H-C_6H_5$
30


$C_6H_5\overset{O}{\overset{\|}{C}}-CHBr_2$
31

If we apply our previously postulated mechanism for the phosphite reactions,[3] *E* phosphates must result from the *irreversible* addition of phosphites to halogen eclipsed or halogen gauche conformers of α-halocarbonyl compounds while the *Z* phosphates are derived from halogen-staggered conformers.[18] While this concept of kinetically controlled carbonyl addition seems especially attractive for α-haloaldehydes which exist as the halogen eclipsed or gauche conformers in the ground state,[19] there are problems with the rationalization of some of the other cases.

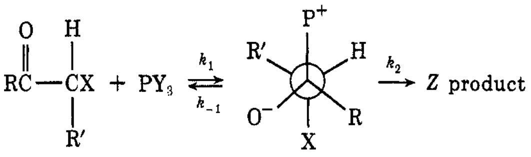


E product vii

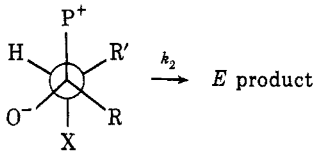


Z product viii

An alternative explanation of the stereochemistry of the Perkow reaction involves the assumption of *reversible* phosphite addition to carbonyl and subsequent thermodynamic control in the elimination step leading to (*E*)- or (*Z*)-vinylphosphonium halides. The elimination is assumed to be anti, and the last step, Arbusov cleavage to the vinyl phosphorylated species, is assumed to be rapid, as already discussed.[3] For cases where the k_2 Cl/Br ratio ≥ 1,[3,6] this may mean that k_2 values are not much greater than k_{-1} or that the initial equilibrium for addition to carbonyl favors the α-chloro ketone while the elimination is faster for bromide loss, as usual.[20,21]



ix



x

Thus the predominance of *E* products (vii, R = H) from α-haloaldehydes and *Z* products (viii) from α-halo ketones may reflect the greater thermodynamic stability of these products *vs.* their stereoisomers.[22]

The tendency toward equilibrium control is seen in comparing the k_2 Br/Cl ratios for the reactions of several α-halo ketones with the series triethyl phosphite (**25**), phosphonite **24**, and phosphinite **23**. Thus the ratios increase from 0.62 to 1.76 for *p*-nitrophenacyl halides and from 1.0 to 7.2 for 2-halocyclohexanones.[6] The predominance of *E* product in the diphenyl phosphinite reactions (as for **26** and **27**, Table VI) may reflect the greater stability of products with the bulky diphenylphosphinoxy group trans to the β-vinyl substituent.

Addition of a phosphinite to carbonyl should give a less stabilized intermediate (xi) than the corresponding phosphite adduct (xii) which can be stabilized by pentacovalency and other factors. Thus the carbonyl additions by phosphinites should tend to be more reversible than those of phosphites and therefore more subject to thermodynamic control.

The reactions of dibromo ketones or halobenzyl phenyl ketones (**29** and **30** in Table VI) with P(III) are not explicable by these arguments. Perkow re-

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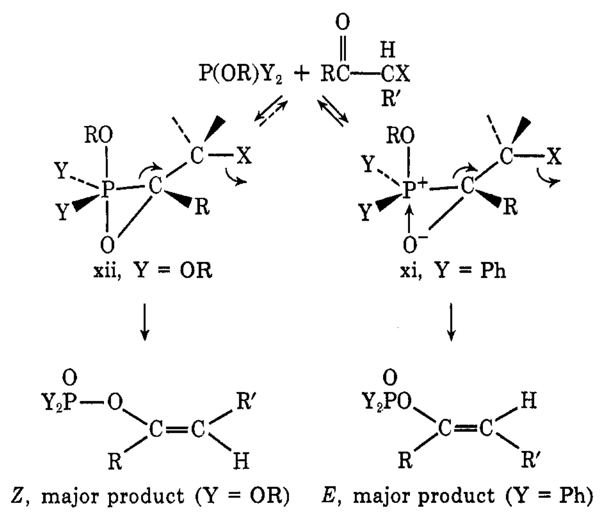
[18] See J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice Hall, Englewood Cliffs, N. J., 1971, Chapter 3, pp 84–116, for an excellent discussion of the stereochemistry of addition of nucleophiles to acyclic ketones and aldehydes.

[19] G. J. Karabatsos and D. J. Fenoglio, *J. Amer. Chem. Soc.*, **91**, 1124 (1969).

[20] The greater inductive effect of chlorine *vs.* bromine may suffice to explain a more favorable equilibrium for carbonyl addition.

[21] The postulate of rate-determining reversible carbonyl addition followed by stereochemistry-determining olefin formation is found in the Wittig reaction: A. J. Speziale and D. E. Bissing, *J. Amer. Chem. Soc.*, **85**, 3878 (1963).

[22] It is assumed that the "effective" size decreases $OPOPh_2 > Ph > OPO(OR)_2$, based on Dreiding models.



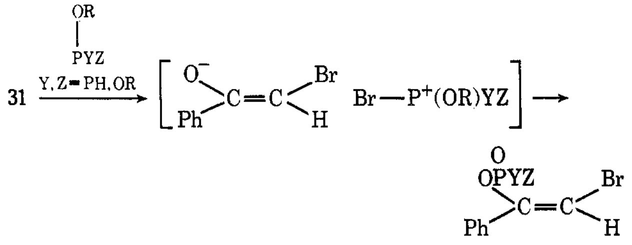
xii, Y = OR

xi, Y = Ph

Z, major product (Y = OR)

E, major product (Y = Ph)

actions of α,α-dibromo ketones are characterized by exclusive formation of *Z* products, debromination in the presence of acetic acid,[6,23] and large k_2 Br/Cl ratios (∼200) *vs.* those of the corresponding dichloroketone.[6] The data suggests that dibromo ketones react with P(III) *via* initial attack on bromine followed by O-phosphorylation of the resultant enolate halophosphonium ion pair. It is noteworthy that the (*Z*)-vinyl phosphate is the sole product formed in the phosphorylation of propiophenone or benzyl phenyl ketone under kinetic or equilibrium control conditions.[2]



The reactions of bromobenzyl phenyl ketone (**30**) with P(III), and possibly even of chlorobenzyl phenyl ketone (**29**) with phosphinites, may also proceed by halogen attack (at least in part). The k_2 Br/Cl ratios for these reactions range from 24 (triethyl phosphite reactions) to 205 (reactions with ethyl diphenylphosphinite),[6] and *Z* products predominate (Table VI).

In summary, Perkow reactions can occur *via* several mechanistic pathways. Evidence on the reversibility or nonreversibility of carbonyl addition in these reactions is needed.

Experimental Section[24]

The vinyl phosphates,[2,3] phosphonates,[2,6] and phosphinates[6,26] have been described. Eu(DPM)$_3$, mp 188–189°, and Pr(DPM)$_3$, mp 218–220°, were purchased from Alfa Inorganics.

General LIS Procedure.—The nmr spectrum of the vinyl phosphorylated species (1–2 × 10^{-4} mol) in dry CCl$_4$ (0.5 ml)–TMS was recorded at 60 MHz. Increments of lanthanide shift reagent were added and spectra recorded. From the slope of the plot of induced chemical shifts *vs.* the mole ratio of LIS reagent/substrate, the magnitude of induced shifts for certain protons in the substrate were calculated. All plots used to determine these shifts were linear over a range of LIS reagent/substrate of 0–0.4.

Registry No.—**1a**, 10409-52-6; **1b**, 10409-53-7; **2a**, 10409-50-4; **2b**, 10409-51-5; **3a**, 31327-17-0; **3b**, 31327-16-9; **4a**, 31428-82-7; **4b**, 31327-18-1; **5**, 31651-16-8; **6**, 38868-16-5; **7**, 38868-17-6; **8**, 38868-18-7; **9**, 38868-19-8; (*E*)-**10**, 31327-12-5; (*Z*)-**10**, 38858-37-6; **11a**, 31327-14-7; **11b**, 31327-15-8; (*E*)-**12**, 31327-13-6; (*Z*)-**12**, 38858-40-1; **13**, 5954-28-9; **14**, 31327-22-7; **15**, 1021-45-0; **16a**, 38858-41-2; **16b**, 38858-42-3; **17**, 30908-58-8; **18**, 10409-55-9; **19a**, 38778-62-0; **19b**, 38778-61-9; **20a**, 31327-10-3; **20b**, 31327-09-0; **22**, 31327-19-2; **23**, 719-80-2; **24**, 3030-90-8; **25**, 122-52-1; **26**, 6084-17-9; **27**, 2114-00-3; **28**, 2648-61-5; **29**, 447-31-4; **30**, 1484-50-0; **31**, 13665-04-8.

Acknowledgments.—We thank Professors S. Sternhell and R. Breslow for stimulating discussions. The hospitality of the Eidgenossische Technische Hochschule, Zurich, which enabled the preparation of part of this paper is gratefully acknowledged. We also thank Professor J. Oth for NOE results and E. Gaydou for unpublished results.

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[23] I. J. Borowitz, S. Firstenberg, E. W. R. Casper, and R. K. Crouch, *Phosphorus*, **1**, 301 (1972).

[24] Instrumental and relevant experimental techniques have been previously described.[3,25]

[25] I. J. Borowitz, K. C. Kirby, P. E. Rusek, and E. W. R. Casper, *J. Org. Chem.*, **36**, 88 (1971).

[26] I. J. Borowitz, E. W. R. Casper, R. K. Crouch, and K. C. Yee, *J. Org. Chem.*, **37**, 3873 (1972).